XXII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CHLORSULPHOPYROMUCIC ACIDS.

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THE sulphonic acids which may be formed by the action of fuming sulphuric acids upon the several brompyromucic acids were described nearly three years ago by Hill and Palmer.* The chlorpyromucic acids, which were at that time unknown, were afterwards studied by Hill and Jackson,† and were shown to differ in certain respects quite essentially from the corresponding bromine derivatives. It therefore seemed to us advisable to study also the behavior of these acids toward fuming sulphuric acid.

β-Chlor-δ-Sulphopyromucic Acid.

β-chlorpyromucic acid dissolves readily in fuming sulphuric acid (sp. gr. 1.95), and the corresponding sulphonic acid is rapidly formed without appreciable carbonization. The β-chlorpyromucic acid itself we prepared by reducing βγ-dichlorpyromucic acid with sodium amalgam containing one per cent of sodium. Complete reduction could be effected by using one and a half times the calculated amount of amalgam, and about fifty per cent of the theoretical yield of β-chlorpyromucic acid was obtained. The β-chlor-δ-sulphopyromucic acid was isolated in the usual way, after neutralizing the diluted acid solution with baric carbonate. The free acid crystallizes in hemispherical masses of indistinct radiating needles, which deliquesce rapidly when exposed to moist air.

Baric β-Chlor-δ-Sulphopyromucate, $BaC_5HClSO_6 . 4H_2O$.

This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallizes in prisms which contain four molecules of

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* These Proceedings, xxiii. 188.   † These Proceedings, xxiv 320.

water.   When exposed to the air it slowly effloresces, and loses its water readily over sulphuric acid or when heated to 100°.

I. 0.7880 grm. of salt dried by short exposure to the air gave 0.4246 grm. $BaSO_4$.

II. 0.6729 grm. air-dried salt gave 0.3631 grm. $BaSO_4$.

III. 1.5568 grm. air-dried salt lost at 100° 0.2547 grm. H_2O.

IV. 1.1932 grm. air-dried salt lost over H_2SO_4 0.1935 grm. H_2O.

	Calculated for $BaC_5HClSO_6 . 4H_2O$.	I.	Found. II.	III.	IV.
Ba	31.60	31.63	31.72		
H_2O	16.61			16.36	16.22

I. 0.6958 grm. salt dried at 100° gave 0.4477 grm. $BaSO_4$.

II. 1.0371 grm. salt dried over H_2SO_4 gave 0.6678 grm. $BaSO_4$.

	Calculated for BaC_5HClSO_6.	Found. I.	II.
Ba	37.89	37.83	37.86

The solubility of the salt in cold water we determined in the usual way.

I. 15.6246 grm. solution saturated at 20° gave 0.1888 grm. $BaSO_4$.

II. 17.2519 grm. solution saturated at 20° gave 0.2084 grm. $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salts : —

I.	II.
1.87	1.87

Plumbic β-Chlor-δ-Sulphopyromucate, $PbC_5HClSO_6 . 4 H_2O$.

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallizes when its hot aqueous solution is cooled in thick rhombic prisms which contain four molecules of water.   The salt effloresces slowly when exposed to the air, loses the greater part of its water over sulphuric acid, and becomes anhydrous when heated to 125°.

I. 0.7342 grm. air-dried salt gave 0.4416 grm. $PbSO_4$.

II. 1.7839 grm. air-dried salt lost at 125° 0.2552 grm. H_2O.

III. 0.7343 grm. air-dried salt lost at 125° 0.1045 grm. H_2O.

	Calculated for PbC_5HClSO_6 $4H_2O$	I	Found. II.	III.
Pb	41.11	41.09		
H_2O	14.30		14.31	14.23

I. 0.6298 grm. salt dried at 125° gave 0.4416 grm. $PbSO_4$.

II. 0.6611 grm. salt dried at 125° gave 0.4634 grm. $PbSO_4$.

	Calculated for PbC_5HClSO_6	Found. I.	II.
Pb	47.97	47.88	47.88

Potassic β-Chlor-δ-Sulphopyromucate, $K_2C_5HClSO_6 . H_2O$.

The potassium salt was readily soluble even in cold water, but was obtained by cooling a hot concentrated aqueous solution in the form of transparent prisms, which effloresced over sulphuric acid.

I. 0.7895 grm. air-dried salt gave 0.4260 grm. K_2SO_4.

II. 1.7840 grm. air-dried salt lost at 110° 0.1104 grm. H_2O.

	Calculated for $K_2C_5HClSO_6 . H_2O$	Found. I.	II.
K	24.39	24.22	
H_2O	5.61		6.18

I. 0.9626 grm. salt dried at 110° gave 0.5464 grm. K_2SO_4.

II. 0.7043 grm. salt dried at 110° gave 0.4003 grm. K_2SO_4.

	Calculated for $K_2C_5HClSO_6$	Found. I.	II
K	25.83	25.48	25.52

While there could be little doubt of the constitution of the sulphonic acid formed from β-chlorpyromucic acid, we attempted to establish more definitely the position of its sulpho group by reducing it to the δ-sulphopyromucic acid. We found, however, that the chlorine was much more firmly held than the bromine of the corresponding β-brom-δ-sulphopyromucic acid, and that the reduction could not be effected by the ordinary reducing agents. Zinc dust in an ammoniacal solution, which had given satisfactory results with the bromsulphopyromucic acids, removed the chlorine so slowly that, even after boiling the solution for days, the reduction was far from complete. On the other hand, sodium amalgam added to the aqueous solution of the barium salt at once attacked the sulpho group, baric sulphite was precipitated, and β-chlorpyromucic acid was formed. With other reducing agents in acid solution we were equally unsuccessful. The ready elimination of the sulpho group by the action of sodium amalgam in alkaline solution was so unexpected that we were led to examine the behavior of other sulphopyromucic acids under the same conditions. We found that δ-sulphopyromucic acid was thus readily reduced to pyromucic acid, while β-sulphopyromucic acid was apparently unaffected, and that

the halogen derivatives of these two acids which we had at our disposal showed precisely the same difference in behavior. The removal of the sulpho group from the chlorsulphopyromucic acid in question may therefore be taken as evidence that the sulpho group is in the δ position.

Action of Bromine.

Like all the derivatives of δ-sulphopyromucic acid which have thus far been examined, β-chlor-δ-sulphopyromucic acid is at once oxidized by bromine in aqueous solution, and sulphuric acid is formed. Bromine was added in slight excess to a solution of the barium salt of the acid, the baric sulphate removed by filtration, and the acid filtrate extracted with ether. The acid thus obtained was very readily soluble in water and practically insoluble in benzol. After recrystallization from water it was dried and washed with benzol. The acid thus purified melted at 188°, and with the quantity at our command we found it impossible to raise this melting point. Although chlorfumaric acid melts at 191°,* there can be no doubt that chlorfumaric acid had been found in the reaction.

Action of Nitric Acid.

Like the brom-δ-sulphopyromucic acids, the β-chlor-δ-sulphopyromucic acid is readily converted into the corresponding nitro-acid by the action of fuming nitric acid. For its preparation we dissolved the dry sulphonic acid in cold fuming nitric acid, warmed the solution for some time upon the water bath, and finally evaporated the nitric acid at a gentle heat. The crystalline product thus obtained was recrystallized first from water, then from benzol, and finally from water. The β-chlor-δ-nitropyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallizes in thick clustered needles. By the slow cooling of the hot solution, or by spontaneous evaporation of the solution, well formed monoclinic (?) prisms with bevelled ends are obtained. The crystallized acid contains one molecule of water, part of which at least it loses over sulphuric acid, and the whole of which may be driven off at 75°. The anhydrous acid melts at 140–141°.

1.4274 grm. air-dried substance lost at 75° 0.1281 grm. H_2O.

	Calculated for $C_5H_2ClNO_5 . H_2O$.	Found.
H_2O	8.59	8.97

* Kauder, Journal für prakt. Chemie, [2.] xxxi. 28.

I. 0.2623 grm. substance dried at 75° gave 0.1970 grm. AqCl.

II. 0.2070 grm. substance dried at 75° gave 13.8 c.c. of moist nitrogen at 25° under a pressure of 762 mm.

	Calculated for $C_5H_2ClNO_5$.	Found. I.	II.
Cl	18.54	18.57	
N	7.31		7.45

$\beta\gamma$-DICHLOR-δ-SULPHOPYROMUCIC ACID.

$\beta\gamma$-dichlorpyromucic acid dissolves without charring in fuming sulphuric acid, and in the course of a few hours is converted into the corresponding sulphonic acid. The barium salt obtained by neutralizing the diluted solution with baric carbonate is quite readily soluble in cold water, but it can be purified without difficulty by recrystallization from hot water. The free acid crystallizes in indistinct radiating needles, and deliquesces rapidly when exposed to the air.

Baric $\beta\gamma$-Dichlor-δ-Sulphopyromucate, $BaC_5Cl_2SO_6 . 5\,H_2O$.

This salt is very readily soluble in hot water, less soluble in cold water, and separates as the hot solution cools in globular aggregations of radiating needles which contain five molecules of water. The salt is permanent in the air, but slowly effloresces over sulphuric acid. It loses a part of its water at 100°, but a temperature of 180° appears to be necessary for complete dehydration.

I. 0.4258 grm. air-dried salt gave 0.2045 grm. $BaSO_4$.

II. 1.0938 grm. air-dried salt gave 0.5239 grm. $BaSO_4$.

III. 1.5844 grm. air-dried salt lost at 185° 0.2930 grm. H_2O.

IV. 0.9712 grm. air-dried salt lost at 190° 0.1792 grm. H_2C.

	Calculated for $BaC_5Cl_2SO_6 . 5H_2O$.	I.	Found. II.	III.	IV.
Ba	28.19	28.23	28.16		
H_2O	18.52			18.49	18.45

I. 1.0167 grm. salt dried at 185° gave 0.5970 grm. $BaSO_4$.

II. 0.6549 grm. salt dried at 190° gave 0.3837 grm. $BaSO_4$.

	Calculated for $BaC_5Cl_2SO_6$.	Found. I.	II.
Ba	34.59	34.52	34.44

The solubility of the salt in cold water was also determined in the usual manner.

I. 18.7100 grm. solution saturated at 18° gave 1.0970 grm. $BaSO_4$.

II. 21.2012 grm. solution saturated at 18° gave 1.2458 grm. $BaSO_4$.

The aqueous solution saturated at 18° therefore contained the following percentages of the anhydrous salt : —

I.	II.
9.97	9.98

Plumbic βγ-Dichlor-δ-Sulphopyromucate, $PbCl_5Cl_2SO_6 . 3 H_2O$.

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and separates on cooling its concentrated aqueous solution in masses of fine needles.

I. 0.5342 grm. air-dried salt gave 0.3106 grm. $PbSO_4$.
II. 0.5524 grm. air-dried salt gave 0.3212 grm. $PbSO_4$.
III. 1.1523 grm. air-dried salt lost at 160° 0.1163 grm. H_2O.
IV. 1.2621 grm. air-dried salt lost at 160° 0.1286 grm. H_2O.

	Calculated for $PbC_5Cl_2SO_6 . 3 H_2O$.	I	II.	III	IV.
			Found.		
Pb	39.81	39.72	39.73		
H_2O	10.39			10.09	10.19

I. 0.4520 grm. salt dried at 160° gave 0.2910 grm. $PbSO_4$.
II. 0.6342 grm. salt dried at 160° gave 0.4107 grm. $PbSO_4$.

	Calculated for $PbC_5Cl_2SO_6$.	I.	II.
		Found.	
Pb	44.42	43.98	44.24

Potassic βγ-Dichlor-δ-Sulphopyromucate, $K_2C_5Cl_2SO_6 . H_2O$.

This salt we made by precipitation with potassic carbonate from the barium salt. It was readily soluble even in cold water, and crystallized in needles which contained one molecule of water. The air-dried salt lost nothing over sulphuric acid.

I. 0.6161 grm. air-dried salt gave 0.3017 grm. K_2SO_4.
II. 0.6722 grm. air-dried salt gave 0.3299 grm. K_2SO_4.
III. 1.4226 grm. air-dried salt lost at 160° 0.0686 grm. H_2O.

	Calculated for $K_2C_5Cl_2SO_6 . H_2O$	I.	II.	III.
			Found.	
K	22.02	21.99	22.04	
H_2O	5.07			4.82

I. 0.6218 grm. salt dried at 160° gave 0.3200 grm. K_2SO_4.
II. 0.7197 grm. salt dried at 160° gave 0.3688 grm. K_2SO_4.

	Calculated for $K_2C_5Cl_2SO_6$	I.	II.
		Found.	
K	23.19	23.10	23.01

The calcium salt of the acid is very soluble even in cold water, and it was not obtained in a crystalline form.

Action of Bromine.

$\beta\gamma$-dichlor-δ-sulphopyromucic acid and its salts are immediately oxidized by bromine in aqueous solution, with the formation of carbonic dioxide, sulphuric acid, and dichlormaleic acid. Baric $\beta\gamma$-dichlor-δ-sulphopyromucate was suspended in water and a slight excess of bromine added. Baric sulphate was at once thrown down, and from the filtered solution dichlormaleic acid was obtained by extraction with ether. From the acid the anhydride was made by sublimation and its identity established through its melting point, 119–120°.*

The formation of $\beta\gamma$-dichlor-δ-nitropyromucic acid through the action of fuming nitric acid has already been described by Hill and Jackson.†

β-Sulpho-δ-Chlorpyromucic Acid.

δ-chlorpyromucic acid was slowly added to four times its weight of fuming sulphuric acid (sp. gr. 1.95), and the solution allowed to stand for ten or twelve hours. The formation of the sulphonic acid was then complete, and on neutralizing the diluted solution with baric carbonate a barium salt was obtained which could easily be purified by recrystallization from hot water. The free β-sulpho-δ-chlorpyromucic acid crystallized in dendritic needles which under ordinary atmospheric conditions are permanent in the air.

Baric β-Sulpho-δ-Chlorpyromucate, $BaC_5HClSO_6 . 5 H_2O$.

This salt is readily soluble in hot water, and but sparingly soluble in cold water. It crystallizes in large radiating needles which are permanent in the air, but slowly loses four of its five molecules of water over sulphuric acid.

  I. 0.8535 grm. air-dried salt gave 0.4411 grm. $BaSO_4$.

  II. 1.6218 grm. air-dried salt gave 0.8371 grm. $BaSO_4$.

  III. 1.9648 grm. air-dried salt lost at 130° 0.3893 grm. H_2O.

  IV. 0.9748 grm. air-dried salt lost at 150° 0.1927 grm. H_2O.

  V. 1.9953 grm. air-dried salt lost at 140° 0.3936 grm. H_2O.

	Calculated for $BaC_5HClSO_6 . 5 H_2O$.	I.	II.	III.	IV.	V.
				Found.		
Ba	30.34	30.38	30.35			
H_2O	19.93			19.81	19.76	19.73

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* Ciamician and Silber, Berichte d. deutsch. chem. Gesellsch., xvi. 2396.

† These Proceedings, xxiv. 361.

1.5355 grm. air-dried salt lost over H_2SO_4 0.2467 grm. H_2O.

	Calculated for $BaC_5HClSO_6 . 5 H_2O$.	Found.
$4 H_2O$	15.95	16.06

I. 1.5480 grm. salt dried at 130° gave 0.9992 grm. $BaSO_4$.
II. 1.2325 grm. salt dried at 140° gave 0.7866 grm. $BaSO_4$.

	Calculated for BaC_5HClSO_6.	Found. I.	II.
Ba	37.89	37.96	37.52

The solubility of the salt in cold water was determined in the usual way.

I. 35.0277 grm. solution saturated at 18° gave 0.3817 grm. $BaSO_4$.
II. 27.2112 grm. solution saturated at 18° gave 0.2985 grm. $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt: —

I.	II.
1.69	1.70

Acid Baric β-Sulpho-δ-Chlorpyromucate, $Ba(C_5H_2ClSO_6)_2 . 4 H_2O$.

This salt was made by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It proved to be quite readily soluble in cold water, much more freely soluble in hot water, and separated on cooling in well formed rhombic prisms which were permanent in the air and lost nothing over sulphuric acid.

I. 0.6413 grm. air-dried salt gave 0.2261 grm. $BaSO_4$.
II. 0.6463 grm. air-dried salt gave 0.2281 grm. $BaSO_4$.
III. 1.7167 grm. air-dried salt lost at 125° 0.1855 grm. H_2O.

	Calculated for $Ba(C_5H_2ClSO_6)_2 . 4 H_2O$.	Found. I.	II.	III.
Ba	20.76	20.72	20.75	
H_2O	10.91			10.81

I. 0.7345 grm. salt dried at 125° gave 0.2900 grm. $BaSO_4$.
II. 0.7734 grm. salt dried at 125° gave 0.3052 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2ClSO_6)_2$	Found I.	II.
Ba	23.30	23.21	23.20

The solubility of the salt in cold water was also determined.

I. 6.7510 grm. solution saturated at 20° gave 0.1935 grm. $BaSO_4$.
II. 5.6625 grm. solution saturated at 20° gave 0.1627 grm. $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt : —

I.	II.
7.23	7.24

Calcic β-Sulpho-δ-Chlorpyromucate, $CaC_5HClSO_6 . 2 H_2O.$

The calcium salt crystallizes in transparent prisms which contain two molecules of water. It is permanent in the air or over sulphuric acid, and requires a high temperature for complete dehydration. The salt dried at 200° showed no signs of decomposition.

I. 0.9321 grm. air-dried salt gave 0.4166 grm. $CaSO_4$.

II. 0.8489 grm. air-dried salt gave 0.3784 grm. $CaSO_4$.

III. 1.6243 grm. air-dried salt lost at 200° 0.1904 grm. H_2O.

	Calculated for $CaC_5HClSO_6 . 2 H_2O$.	I.	Found. II.	III.
Ca	13.31	13.14	13.11	
H_2O	11.98			11.72

I. 0.5804 grm. salt dried at 200° gave 0.2956 grm. $CaSO_4$.

II. 0.7000 grm. salt dried at 200° gave 0.3566 grm. $CaSO_4$.

	Calculated for CaC_5HClSO_6	I.	Found. II.
Ca	15.12	14.98	14.98

Plumbic β-Sulpho-δ-Chlorpyromucate, $PbC_5HClSO_6 . H_2O.$

This salt is sparingly soluble in cold water, more readily soluble in hot water, and crystallizes in compact clusters of radiating prisms. It loses nothing over sulphuric acid, or when heated to 100°.

I. 0.5646 grm. air-dried salt gave 0.3799 grm. $PbSO_4$.

II. 0.6672 grm. air-dried salt gave 0.4485 grm. $PbSO_4$.

III. 1.6403 grm. air-dried salt lost at 165° 0.0705 grm. H_2O.

IV. 1.5787 grm. air-dried salt lost at 160° 0.0631 grm. H_2O.

V. 1.6982 grm. air-dried salt lost at 160° 0.0629 grm. H_2O.

	Calculated for $PbC_5HClSO_6 . H_2O$.	I.	II.	Found. III.	IV.	V.
Pb	46.06	45.95	45.93			
H_2O	4.00			4.29	3.99	3.70

I. 0.5240 grm. salt dried at 165° gave 0.3690 grm. $PbSO_4$.

II. 1.0133 grm. salt dried at 160° gave 0.7118 grm. $PbSO_4$.

III. 0.5399 grm. salt dried at 160° gave 0.3791 grm. $PbSO_4$.

	Calculated for PbC_5HClSO_6.	I.	Found. II.	III.
Pb	47.98	48.10	48.01	47.96

Potassic β-Sulpho-δ-Chlorpyromucate, $K_2C_5HClSO_6$.

The potassium salt crystallizes in long needles which are anhydrous.

I.   0.9272 grm. air-dried salt gave 0.5309 grm. K_2SO_4.
II. 0.8955 grm. air-dried salt gave 0.5126 grm. K_2SO_4.
III. 0.7962 grm. air-dried salt gave 0.4562 grm. K_2SO_4.

	Calculated for $K_2C_5HClSO_6$.	I.	Found. II.	III.
K	25.84	25.70	25.70	25.73

Although there could be little doubt that the sulphonic acid formed from δ-chlorpyromucic acid was identical in structure with the β-sulpho-δ-brompyromucic acid of Hill and Palmer,[*] we wished to prove this identity more rigorously by preparing from it by reduction the β-sulphopyromucic acid. We found that the method employed by Hill and Palmer in the reduction of the bromine compound could successfully be employed in this case, although the chlorine was replaced with much greater difficulty, and long continued boiling of the ammoniacal solution with zinc dust was essential for complete reduction. We also found it advantageous to convert the baric β-sulpho-pyromucate into the acid salt, and to purify this by recrystallization from hot water. The neutral salt was crystallized for analysis by evaporation *in vacuo* over sulphuric acid.

I. 0.7039 grm. air-dried salt gave 0.4287 grm. $BaSO_4$.
II. 1.0434 grm. air-dried salt lost at 160° 0.1476 grm. H_2O.

	Calculated for $BaC_5H_2SO_6 . 3H_2O$.	I.	Found. II.
Ba	35.96	35.80	
H_2O	14.18		14.15

0.8946 grm. salt dried at 160° gave 0.6347 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found.
Ba	41.90	41.72

The solubility of the salt in cold water was determined by the usual method.

I. 14.4785 grm. solution saturated at 21° gave 0.1960 grm. $BaSO_4$.
II. 12.0525 grm. solution saturated at 21° gave 0.1628 grm. $BaSO_4$.

The solution saturated at 21° therefore contained the following percentages of the anhydrous salt: —

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[*] These Proceedings, xxiii. 214.

<div style="text-align:center">

I.   II.

1.90   1.90

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These results agree exactly with those obtained by Hill and Palmer for β-sulphopyromucic acid, and the relative position of the sulpho group is thus established with precision.

Action of Bromine.

β-sulpho-δ-chlorpyromucic acid is readily oxidized in aqueous solution by bromine, carbonic dioxide is liberated, but little or no sulphuric acid is formed even when the action is long continued at 100°. With an excess of bromine, an acid is formed which is undoubtedly identical with the sulphofumaric acid described by Hill and Palmer,* while a derivative of furfuran-β-sulphonic acid is formed in nearly theoretical quantity, if but a single molecule of bromine is added. For its preparation we passed into a cold aqueous solution of baric β-sulpho-δ-chlorpyromucate the vapor of the calculated weight of bromine by means of a current of air, and evaporated to a small volume the feebly acid solution thus obtained. The barium salt of the $\alpha\alpha$-chlorbrom-furfuran-β-sulphonic acid which was thus obtained could then be purified by recrystallization. By evaporation in desiccator the free acid was obtained as a waxy deliquescent mass, which showed but slight indications of crystalline structure.

Baric $\alpha\alpha$-Chlorbromfurfuran-β-Sulphonate, $Ba(C_4HClBrSO_4)_2 . H_2O$.

This salt is readily soluble in hot water, less soluble in cold water, and separates in pearly plates when its hot solution is quickly cooled. A cold solution by spontaneous evaporation deposits this salt in clusters of radiating needles.

I. 0.8479 grm. air-dried salt gave 0.2936 grm. $BaSO_4$.

II. 0.5210 grm. air-dried salt gave 0.1797 grm. $BaSO_4$.

III. 1.1406 grm. air-dried salt lost at 120° 0.0314 grm. H_2O.

IV. 1.6890 grm. air-dried salt lost at 138° 0.0491 grm. H_2O.

	Calculated for $Ba(C_4HClBrSO_4)_2 . H_2O$.	I.	II.	III.	IV.
			Found.		
Ba	20.27	20.35	20.28		
H_2O	2.66			2.75	2.90

I. 0.7017 grm. salt dried at 138° gave 0.2496 grm. $BaSO_4$.

II. 0.9112 grm. salt dried at 138° gave 0.3259 grm. $BaSO_4$.

III. 0.7824 grm. salt dried at 130° gave 0.2795 grm. $BaSO_4$.

* These Proceedings, xxiii. 211.

	Calculated for Ba(C$_4$HClBrSO$_4$)$_2$.	Found. I.	II.	III.
Ba	20.82	20.92	21.03	21.00

The solubility of the salt in cold water was also determined in the usual way.

I. 20.5274 grm. solution saturated at 18° gave 0.3105 grm. BaSO$_4$.
II. 21.5098 grm. solution saturated at 18° gave 0.3276 grm. BaSO$_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:—

I.	II.
4.27	4.30

Calcic aa-Chlorbromfurfuran-β-Sulphonate, Ca(C$_4$HClBrSO$_4$)$_2$. 2 H$_2$O.

The calcium salt crystallizes in large concentrically grouped needles which contain two molecules of water. It is permanent in the air or over sulphuric acid.

I. 0.6429 grm. air-dried salt gave 0.1480 grm. CaSO$_4$.
II. 0.7372 grm. air-dried salt gave 0.1702 grm. CaSO$_4$.
III. 0.7580 grm. air-dried salt lost at 160° 0.0468 grm. H$_2$O.

	Calculated for Ca(C$_4$HClBrSO$_4$)$_2$. 2 H$_2$O.	Found. I.	II.	III.
Ca	6.70	6.77	6.79	
H$_2$O	6.03			6.17

I. 0.4463 grm. salt dried at 160° gave 0.1097 grm. CaSO$_4$.
II. 0.4230 grm. salt dried at 165° gave 0.1045 grm. CaSO$_4$.

	Calculated for Ca(C$_4$HClBrSO$_4$)$_2$.	Found. I.	II.
Ca	7.13	7.23	7.26

Plumbic aa-Chlorbromfurfuran-β-Sulphonate, Pb(C$_4$HClBrSO$_4$)$_2$. H$_2$O.

The lead salt is but sparingly soluble in cold water, and its solubility is but little increased by heat. By evaporation *in vacuo* over sulphuric acid it was obtained in compact hemispherical masses. The salt may be dried without decomposition at 100°, but at a somewhat higher temperature it begins to decompose, and at 140° it is completely charred.

I. 0.5743 grm. air-dried salt gave 0.2339 grm. PbSO$_4$.
II. 1.5077 grm. air-dried salt lost at 100° 0.0410 grm. H$_2$O.

	Calculated for Pb(C$_4$HClBrSO$_4$)$_2$. H$_2$O.	Found. I.	II.
Pb	27.75	27.83	
H$_2$O	2.41		2.72

0.7187 grm. salt dried at 100° gave 0.3000 grm. PbSO$_4$.

	Calculated for Pb(C$_4$HClBrSO$_4$)$_2$.	Found.
Pb	28.39	28.52

Potassic aa-Chlorbromfurfuran-β-Sulphonate, KC$_4$HClBrSO$_4$.

The potassium salt is very soluble in hot water, less soluble in cold water. The hot concentrated solution solidifies on cooling, with the separation of small shining anhydrous plates.

I. 0.5801 grm. air-dried salt gave 0.1699 grm. K$_2$SO$_4$.
II. 0.5479 grm. air-dried salt gave 0.1625 grm. K$_2$SO$_4$.

	Calculated for KC$_4$HClBrSO$_4$.	Found I.	II.
K	13.05	13.15	13.31

Action of Chlorine.

We attempted to prepare aa-dichlorfurfuran-β-sulphonic acid by the action of chlorine upon the salts of β-sulpho-δ-chlorpyromucic acid. We found, however, that the reaction in this case was not as simple as that with bromine, in that the oxidation of the furfuran-sulphonic acid began long before one molecule of chlorine had been added, and that sulphofumaric acid and even sulphuric acid were formed before the whole of the original sulphochlorpyromucic acid had disappeared. While it was not difficult to isolate a salt which had substantially the properties and the composition of a baric dichlorfurfuran sulphonate, we were unable to prepare by any variation of the method a product from which we could obtain perfectly satisfactory results.

Action of Nitric Acid.

We studied the action of nitric acid upon β-sulpho-δ-chlorpyromucic acid only so far as to satisfy ourselves that no nitro-acid could be formed in this way, and that sulphofumaric acid was the chief product of the reaction.